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An Experimental Estimate of the Electron-Tunneling

Distance for Some Outer-Sphere Electrochemical Reactions

by

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AN EXPERIMENTAL ESTIMATE OF THE ELECTRON-TUNNELING
DISTANCE FOR SOME OUTER-SPHERE ELECTROCHEMICAL REACTIONS

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Abstract

Estimates of the reaction zone thickness over which electron tunneling can effectively occur for the outer-sphere electrochemical reduction of some Cr(III) complexes are obtained by comparing the observed work-corrected rate constants with unimolecular rate constants for the electroreduction of structurally similar surface-bound Cr(III) reactants. Effective reaction zone thicknesses of ca 0.1 - 0.3 $\mathring{A}$ and ca 5 $\mathring{A}$ are obtained for outer-sphere electron transfer with Cr(III) reactants containing predominantly aquo or ammine ligands, respectively. This indicates that the former reactions are marginally nonadiabatic whereas the latter are decidely adiabatic at their respective planes of closest approach. These findings are compatible with the greater reactant-electrode separation distances previously noted for Cr(III) aquo relative to ammine complexes resulting from the more extensive hydration sheath surrounding the former reactants. Comparisons with recent calculations performed for some outer-sphere homogeneous reactions suggest that efficient electron tunneling takes place over roughly comparable distances at metal-electrolyte interfaces and in bulk solution.

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An important question in the treatment of electron-transfer reactions concerns the magnitude of the frequency factor, A, in the expression

$$k_{ob} = A \exp(-w_p/RT) \exp(-\Delta G_{et}^*/RT) \qquad (1)$$

where k_{ob} is the observed rate constant, w_p is the work required to bring the reactants together (or the reactant to the electrode surface), and ΔG_{et}^* is the free-energy barrier for the elementary electron-transfer step. Although sophisticated theoretical methods have been developed for evaluating ΔG_{et}^* from structural and thermodynamic information, there remains considerable uncertainty as to the numerical values of the frequency factor for outer-sphere pathways.[1,2]

In the recent literature it has been emphasized that outer- as well as inner-sphere redox reactions in homogeneous solution and at electrode surfaces can usually be viewed as involving formation of a reactive precursor complex from initially separated reactants followed by the rate-determining transfer step.[1-5] Thus the observed rate constant can be formulated as

$$k_{ob} = K_p k_{et} \qquad (2)$$

where K_p is the equilibrium constant for forming the precursor state and k_{et} is the rate constant describing the elementary electron-transfer step. When applied to outer-sphere pathways, this approach can be termed an "encounter preequilibrium" treatment. It views the reaction as taking place via the unimolecular activation of a weakly interacting reactant pair having a suitably close proximity and geometrical configuration to enable electron transfer to occur once the appropriate nonequilibrium nuclear configuration has been achieved.[1b,c,2b,5c]

According to the encounter-preequilibrium treatment, the frequency factor can be expressed as[1b,c,5c]

$$A = \Gamma_n \nu_n \kappa_{el}^0 K_0 \qquad (3)$$

where Γ_n is the nuclear tunneling factor, ν_n is the effective frequency for activating nuclear reorganization modes, κ_{el}^0 is the electronic transmission coefficient at the distance of closest approach of the reactants and K_0 is the statistical part of the precursor stability constant K_p where

$$K_p = K_0 \exp(-w_p/RT) \qquad (4)$$

For electrochemical reactions the statistical factor K_0^e can be expressed simply as[5c]

$$K_0^e = \delta r_e \qquad (5)$$

where δr_e is the thickness of a "reaction zone" beyond the plane of closest approach within which the reactant must reside in order to contribute significantly to the overall reaction rate. The value of δr_e is determined by the need for the reactant and surface to be in sufficiently close proximity to achieve significant overlap of donor and acceptor orbitals, and hence nonzero values of the transmission coefficient κ_{el} for a given reactant orientation (vide infra). The composite term $\kappa_{el}^0 K_0^e$ ($\equiv \kappa_{el}^0 \delta r_e$) appearing in Eq (3) for electrochemical reactions can therefore be considered to be an "effective reaction zone thickness". If $\kappa_{el}^0 < 1$, the reaction is termed "nonadiabatic", whereas "adiabatic" processes are those for which $\kappa_{el}^0 \sim 1$. Since the magnitude of δr_e is determined by the dependence of κ_{el} upon the donor-acceptor separation distance, markedly

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smaller values of $\kappa_{el}^0 \delta r_e$ are anticipated for the former compared to the latter processes as a result of smaller values of δr_e as well as κ_{el}^0.

The statistical factor for homogeneous reactions, K_o^h, is more complex than K_o^e yet entirely analogous, corresponding to the probability of finding one reactant within a reaction zone of thickness δr_h beyond the bimolecular contact distance. This term can be estimated approximately from[1c,e,2b,c]

$$K_o^h = 4\pi N \bar{r}^2 \delta r_h / 10^3 \tag{6}$$

where N is the Avogadro number, and $\bar{r}$ is the distance between the reacting centers when in contact.

Recent ab initio calculations for some homogeneous outer-sphere reactions[2] indicate that κ_{el} can be substantially below unity even at a relatively small internuclear separation r, decreasing sharply with increasing r. This corresponds to relatively small values of $\kappa_{el}^0 \delta r_h$ (<1Å, vide infra).[1c,e] It would be extremely desirable to obtain an experimental measure of such quantities. In the approach described here, estimates of $\kappa_{el}^0 \delta r_e$ for several outer-sphere electrochemical processes are obtained by a relatively direct method involving the comparison of rate constants for these pathways with those for structurally related electrochemical reactions occuring via geometrically well-defined ligand-bridged transition states. The results provide evidence that heterogeneous, as well as homogeneous, electron-transfer processes can be significantly nonadiabatic.

Data Analysis

The virtue of comparing rate parameters for corresponding electrochemical reactions occuring via outer- and inner-sphere (ligand-bridged) pathways can be seen by noting that in contrast to the former, unimolecular rate constants for the electron-transfer step involving a ligand-bridged precursor state,

k_{et}^{is}(sec^{-1}), can often be determined directly from the overall rate constant, k_{ob}^{is}, using Eq (2) since K_p can be found from[5a,c]

$$K_p = \Gamma_p/C_b \qquad (7)$$

where Γ_p is the measured reactant surface concentration (mole cm^{-2}) corresponding to a given bulk reactant concentration C_b. The values of k_{et}^{is} can be expressed as

$$k_{et}^{is} = \Gamma_n \nu_n \kappa_{el}^{is} \exp(-\Delta G_{et}^{\star}/RT) \qquad (8)$$

where κ_{el}^{is} is the electronic transmission coefficient for the ligand-bridged reaction pathway. In view of Eqs (1) and (3)-(5), the work-corrected rate constant for the corresponding outer-sphere electrochemical pathway, k_{corr}^{os}, can be expressed as

$$k_{corr}^{os} = \Gamma_n \nu_n \kappa_{el}^{os} \cdot \delta r_e \cdot \exp(-\Delta G_{et}^{\star}/RT) \qquad (9)$$

Provided that $\Delta G_{et}^{\star}$, Γ_{el}, and ν_n are unaffected by surface attachment at a given electrode potential (vide infra), evaluation of the rate ratios $k_{corr}^{os}/k_{et}^{is}$ enable estimates of $\kappa_{el}^{o}\delta r_e$, at least relative to κ_{el}^{is}, to be obtained. This procedure will now be utilized to estimate the effective electron-tunneling distances for some outer-sphere Cr(III) reductions at the mercury-aqueous interface.

Pertinent kinetic and thermodynamic data are assembled in Table I for the electroreduction of three Cr^{III}(NH$_3$)$_5$X complexes, where X = NCS$^-$, N$_3^-$, and Cl$^-$, and five Cr^{III}(OH$_2$)$_5$X complexes, where X = OH$_2$, SO$_4^{2-}$, F$^-$, NCS$^-$, and N$_3^-$. The data were extracted from refs 5a, 6, and 7. These reactions where chosen because rate constants corresponding to both inner- and outer-sphere pathways, k_{et}^{is} and k_{corr}^{os} respectively, can be obtained directly

or estimated from experimental data.[5c] Several of these reactions have been examined previously in a related discussion of the relative energetics of inner- and outer-sphere pathways.[5a]

The work-corrected rate constants, k_{corr}^{os}, were determined from the corresponding observed rate constants, k_{ob}^{os}, using the electrostatic double-layer corrections as outlined in ref. 6 (see footnotes to Table I). Of the three Cr(III) ammine reactants, $Cr(NH_3)_5N_3^{2+}$ and $Cr(NH_3)_5Cl^{2+}$ exhibit mixed electroreduction kinetics which enable both k_{ob}^{os} and k_{ob}^{is} to be obtained.[5a,6] The latter values are combined with estimates of K_p obtained under the same conditions from kinetic probe measurements[5a,8] to yield values of k_{et}^{is} by using Eq (2). The common electrode potential of -600 mV vs. the saturated calomel electrode (sce) was chosen so to minimize the extent of data extrapolation that is involved. The estimate of k_{et}^{is} for $Cr(NH_3)_5N_3^{2+}$ reduction (1 sec^{-1}) is close to that observed for $Cr(NH_3)_5NCS^{2+}$ reduction (0.5 sec^{-1}); this supports the validity of the former estimate in view of the closely similar coordination properties of $-N_3^-$ and $-NCS^-$.[5a]

Each of the five Cr(III) aquo reactants in Table I undergoes electro- reduction via sufficiently rate-dominating outer- or inner-sphere pathways so that only k_{ob}^{os} or k_{et}^{is} can be evaluated for each reactant. Nevertheless, an approximate estimate of $k_{corr}^{os}/k_{et}^{is}$ for these structurally related reactions can still be obtained as follows. As we have noted previously,[7] the values of k_{corr}^{os} for $Cr(OH_2)_6^{3+}$, $Cr(OH_2)_5SO_4^+$, and $Cr(OH_2)_5F^{2+}$ reduction are closely similar when evaluated at their respective formal potentials. This indicates that the intrinsic electron-transfer barrier is approximately independent of the nature of the sixth ligand, even though the coordinating properties of OH_2, SO_4^{2-} and F^- differ widely. These values of k_{corr}^{os}, listed in Table I, are therefore also likely to be close to those for $Cr(OH_2)_5NCS^{2+/+}$ and $Cr(OH_2)_5N_3^{2+/+}$

which cannot be measured but for which the corresponding values of k_{et}^{is} are known, enabling the desired estimate of $k_{corr}^{os}/k_{et}^{is}$ to be obtained (Table I).

Discussion

Inspection of Table I shows that the resulting values of $k_{corr}^{os}/k_{et}^{is}$ for Cr(III) aquo reduction, ca. 0.2 Å, are ca. 10-30 fold smaller than those for the Cr(III) ammine reductions, ca 5 Å. Quantitative interpretation of these results can be made by referring to Eqs (8) and (9). Of the various terms, ν_n and Γ_n will almost certainly have the same values for the corresponding inner- and outer-sphere pathways. Thus ν_n is determined chiefly by the metal-ligand stretching frequencies[5c] and Γ_n is usually close to unity, being dependent upon the magnitude of ΔG_{et}^* rather than the transition-state geometry.[1b] The reorganization energy ΔG_{et}^* may differ significantly for corresponding inner- and outer-sphere pathways, arising both from differences in the inner-shell (metal-ligand) and outer-shell (solvent) reorganization terms. Ligand bridging may yield some decreases in the inner-shell component of ΔG_{et}^* arising from the influence of surface attachment on the Cr(III)-ligand bonding. However, we have found scant evidence for such catalyses with Cr(III)/(II) and Co(III)/(II) electrode reactions, even at surfaces such as platinum and gold that bind inorganic ligand bridges much more strongly than does mercury.[9]

Surface attachment may yield an alteration in the outer-shell component of ΔG_{et}^* since this is predicted to diminish as the distance between the redox center and the surface decreases, as a result of greater image stabilization of the transition state.[11] With the azido and isothiocyanato bridges, the redox center is estimated to lie about 5-6 Å from the surface.[10] Provided that the outer-sphere transition state is formed with the reactant in contact with a monolayer of inner-layer water molecules (vide infra), the redox center will

be   about 6.5 Å from the surface, based on a reactant crystallographic radius
of 3.5 Å and a water molecule diameter of 3 Å.[6] On the basis of the well-known
relation for the outer-shell component of ΔG^*_{et} due to Marcus,[11,12] k^{os}_{corr} is
predicted to increase by only ca. 50% upon decreasing the reactant-electrode
separation from 7 to 6 Å, and by only ca 3-fold from 7 to 5 Å. It therefore
appears likely that ΔG^*_{et} only differs to a small extent between corresponding
outer- and inner-sphere pathways involving thiocyanate c .zide bridges.
The similar values of $k^{os}_{corr}/k^{is}_{et}$ seen for $Cr(NH_3)_5Cl^{2+}$ a $Cr(NH_3)_5N_3^{2+}$ reduction
(Table I), even though the Cr(III) - surface distance   xpected to be
ca. 2 Å smaller for the former reaction, lends support L .his assertion.

To a first approximation, then, from Eqs (8) and (9) the rate ratios
$k^{os}_{corr}/k^{is}_{et}$ for the present system can be related to the effective reaction
zone   thickness   for the outer-sphere pathways, $\kappa^0_{el}\delta r_e$, simply by

$$k^{os}_{corr}/k^{is}_{et} \approx \kappa^0_{el}\,\delta r_e/\kappa^{is}_{el} \qquad (10)$$

Since the ligand bridge should facilitate overlap between the surface
donor and Cr(III) acceptor orbitals it is anticipated that the inner-
sphere pathways are adiabatic, i.e. $\kappa^{is}_{el} \sim 1$. If indeed $\kappa^{is}_{el} \sim 1$,
then the values of $k^{os}_{corr}/k^{is}_{et}$, ca 5 Å and 0.2 Å, can be identified directly
with the effective reaction zone thickness $\kappa^0_{el}\delta r_e$ for the ammine and
aquo reactants, respectively. Even if $\kappa^{is}_{el} < 1$, it is likely to have
essentially the same value for both pentaammine- and pentaaquo Cr(III)
reductions bridged by azide and isothiocyanato ligands since the Cr(III)-surface
distance and hence the degree of orbital overlap should be determined by
the bridging ligand. It therefore appears certain that $\kappa^0_{el}\delta r_e$ is markedly
larger for the ammine compared to the aquo reactants.

A persuasive explanation for this striking result is to be found in the differences in the location of the outer-sphere reaction sites that have been noted previously for these reactions.[6,12,13] Thus the reduction rates of $Cr(OH_2)_6^{3+}$ and other Cr(III) aquo complexes are markedly less sensitive to variations in the double-layer potential profile than are the reduction rates of $Cr(NH_3)_6^{3+}$ and related Cr(III) ammines.[6] These results provide evidence that the Cr(III) aquo reaction sites are constrained to lie significantly further from the electrode surface. This is consistent with the larger hydrated radii for aquo versus ammine reactants due to the more extensive ligand-solvent hydrogen bonding exhibited by the former complexes.[6,14] From an analysis of the observed double-layer effects, we have estimated that the reaction site for $Cr(OH_2)_6^{3+}$ reduction lies 6-7 $\mathring{A}$ from the surface, whereas that for $Cr(NH_3)_6^{3+}$ reduction is about 1.5 $\mathring{A}$ closer.[6] (Although the absolute reactant-electrode distances are subject to as much as 1 - 1.5 $\mathring{A}$ uncertainty, the relative distances for the aquo versus ammine reactants are rather more reliable). It is therefore to be expected that κ_{el}^o will be larger for the ammine than for the aquo reactants unless the reactant-surface electronic coupling is sufficient to provide adiabatic pathways ($\kappa_{el}^o \approx 1$) in both cases.

In order to interpret the individual values of $\kappa_{el}^o \delta r_e$, it is advantageous to consider the encounter preequilibrium treatment in a little more detail. Since κ_{el} will depend upon the donor-acceptor separation distance within the reaction zone of thickness δr_e, strictly speaking one should express the overall observed rate constant in terms of an integral of "local" values of k_{et}, each being associated with a particular spatial position and orientation of the reactant and hence individual values of κ_{el}, w_p, and ΔG_{et}^*.[2b] The dependence of κ_{el} upon the separation distance, r, for nonadiabatic pathways

can be approximated by[2a,c]

$$\kappa_{el}(r) = \kappa_{el}^0 \ exp[-\alpha(r-\sigma)] \qquad (11)$$

where σ is the separation distance corresponding to closest approach, and α is a constant which is typically estimated to lie in the range ca. $1 - 2 \ Å^{-1}$.[2c,15] Consequently, if $\kappa_{el}^0 < 1$ (i.e. the reaction is nonadiabatic at the plane of closest approach), the effective value of δr_e will be equal α^{-1}. On the other hand, if σ is sufficantly small so that $\kappa_{el} \simeq 1$ not only at the distance of closest approach but also for a significant distance, χ, beyond it, we expect that roughly

$$\delta r_e \simeq \chi + \alpha^{-1} \qquad (12)$$

Equation (12) therefore provides a general relationship where $\chi = 0$ if $\kappa_{el}^0 < 1$, and $\chi > 0$ if $\kappa_{el}^0 \simeq 1$.

Figure 1 is a schematic representation of the dependence of κ_{el} upon r. The magnitude of $\kappa_{el}^0 \delta r_e$ will equal the area under the curve bounded by the distance of closest approach, for example the shaded area A'A"C. Taking $\alpha \simeq 1.5 \ Å^{-1}$, it follows that $\kappa_{el}^0 \delta r_e < 0.5 \ Å$ if $\kappa_{el}^0 < 1$, whereas $\kappa_{el}^0 \delta r_e > 0.5 \ Å$ if $\kappa_{el}^0 \simeq 1$. The above estimate of $\kappa_{el}^0 \delta r_e$ for the Cr(III) aquo reactions, ca 0.1 - 0.3 Å, therefore suggests that $\kappa_{el}^0 < 1$ at the plane of closest approach for the aquo cations, so that $\chi \approx 0$. However, this estimate of $\kappa_{el}^0 \delta r_e$ may be ca 1.5 to 2-fold too small as a result of the likely differences in ΔG_{et}^* between the inner- and outer-sphere pathways noted above, although it may be too large if $\kappa_{el}^{is} < 1$. Another factor which would decrease the apparent value of $\kappa_{el}^0 \delta r_e$ is the possibility that a

specific reactant orientation is required either to enable the reactant
to approach the electr⁴e more closely or to provide more effective
coupling of the surface donor and Cr(III) acceptor orbitals. Such
factors have recently been considered in detail for $Fe(OH_2)_6^{3+/2+}$ self
exchange.[2] In any case, we conclude that outer-sphere electron transfer
involving the Cr(III) aquo reactants only approaches adiabaticity for
electron-tunneling distances very close to the plane of closest approach
of these cations (represented by B'B" in Fig. 1), around 6-7 $\overset{o}{A}$ from the
electrode surface.

On the other hand, the estimate of $\kappa_{el}^0 \delta r_e$ for the Cr(III) ammines,
ca 5 $\overset{o}{A}$, suggests that electron transfer to these reactants remains adiabatic even
for reaction sites several Angstroms from the plane of closest approach
(represented by A'A" in Fig. 1). The exact value of $\kappa_{el}^0 \delta r_e$ for the ammine
reactants is in one respect subject to greater uncertainty than for the aquo
reactants in that the magnitude of the work-term ("double-layer") correction upon
k_{ob} is somewhat greater for the former.[6] Moreover, the work-term correction
employed assumes that the reaction occurs only at the outer Helmholtz plane
(oHp), whereas the large value of $\kappa_{el}^0 \delta r_e$ suggests that the effective reaction
zone is relatively thick. Given that the ammine reactants can probably
penetrate inside the oHp, this work-term correction may well be an under-
estimate, so that k_{corr}^{os} and hence $\kappa_{el}^0 \delta r_e$ are actually smaller than the present
values. Given that the aquo reactants are marginally adiabatic at their
plane of closest approach, from the reaction site differences noted above
it would be expected that $\chi \sim 2$ $\overset{o}{A}$ for the ammines, yielding $\kappa_{el}^0 \delta r_e \sim$ 2-3 $\overset{o}{A}$.
One factor which may enhance $\kappa_{el}^0 \delta r_e$ for the ammine versus the aquo
complexes is the likely greater ligand character of the acceptor orbital
on the former reactants,[2c] leading to greater electrode-reactant orbital
overlap at a given electrode-reactant separation distance. The
difference in the effective reaction zone thickness between the aquo

and amine reactants is therefore roughly compatible with the likely differences in the reaction sites if the dependence of κ_{el} upon the surface-reactant separation is similar for these reactants, with κ_{el} decreasing below unity for surface-reactant separations greater than ca. 6 Å.

Taking Γ_n = 2.5 and ν_n = 1.2 x 10^{13} sec^{-1} for the present reactions,[16] it is deduced from Eqs (3) and (5) that the overall frequency factor A is ca. 6 x 10^4 and 1.5 x 10^6 cm sec^{-1} for the aquo and amine reactants, respectively. Both these values are somewhat larger than the frequency factor, ca. 5 x 10^3 cm sec^{-1}, derived from the conventional collisional model assuming adiabatic behavior.[5c,17] It should be noted that the encounter preequilibrium treatment employed here represents a departure from the collisional model since the latter views the reaction as being consumated only by collisions between the reactant and the electrode surface (or a coreactant).[5c]

It is of interest to compare the above estimate of A for the Cr(III) aquo reactants with that obtained for $Cr(OH_2)_6^{3+}$ reduction under the same conditions from the temperature dependence of k_{corr}^{os}. We can write[17]

$$k_{corr}^{os} = A \exp(\Delta S_i^*/R) \exp(-\Delta H_i^*/RT) \qquad (13)$$

where ΔS_i^* and ΔH_i^* are the work-corrected "ideal" entropies and enthalpies of activation which form the components of ΔG_{et}^* at the particular electrode potential at which k_{corr}^{os} is obtained.[17,18] The activation enthalpy ΔH_i^* can be obtained directly from the Arrhenius slope of ln k_{corr}^{os} versus (1/T), being measured at a constant electrode potential using a nonisothermal cell arrangement.[17] The value of ΔS_i^* can be obtained from[17,19]

$$\Delta S_i^* = \alpha_{corr}\Delta S_{rc}^{\circ} + \Delta S_{int}^* \qquad (14)$$

where α_{corr} is the work-corrected transfer coefficient, ΔS_{rc}° is the so-called

reaction entropy of the redox couple concerned,[14a] and ΔS_{int}^* is the intrinsic activation entropy.[20] From the data given in ref 17, at -800 mV vs. sce, k_{corr}^{os} = 5.5 x 10^{-5} cm sec^{-1} (25°C), ΔH_i^* = 17.5 kcal. mol^{-1},[21] α_{corr} = 0.50, ΔS_{rc}^o = 49 cal. deg^{-1} mol^{-1}, and ΔS_{int}^* = -3.5 cal. deg^{-1} mol^{-1}.[20] Inserting these data into Eqs (13) and (14) yields A = 9 x 10^3 cm sec^{-1}. (This calculation cannot be performed for Cr(III) ammine reductions since the ΔS_{rc}^o values are not known with sufficient accuracy.)

The ca 7-fold discrepancy between this and the above estimate of A probably arises in part from the very approximate nature of Eq (14). This relation presumes that the transition-state entropy is unaffected by the proximity of the reacting ions to the electrode surface, whereas it is likely that ΔS_i^* and ΔH_i^* are much more sensitive than is the overall barrier ΔG_{et}^* to the solvating environment at the interface and the bulk solution. Indeed, we have found that the activation parameters for these and other reactions are rather more sensitive than is k_{corr}^{os} to the nature of the electrode material, surprisingly small frequency factors being typically obtained at solid metal surfaces.[22]

Conclusions

The foregoing treatment provides a relatively direct, albeit approximate, experimental method for evaluating the effective electron-tunneling distances for outer-sphere electrochemical reactions. It exploits both the close relationship between the energetics of corresponding inner- and outer-sphere electrode reactions and the information that can be derived[6,13] on the reactant-electrode separation distance from the magnitude of the double-layer effects in electrochemical kinetics. A strictly analogous approach cannot be employed for homogeneous processes due to the inevitable changes in reactant coordination between otherwise related inner-

and outer-sphere pathways and the lack of a means for subtly altering
the electrostatic interactions between ionic reactants in solution.

Although it would not be surprising if similar differences in the
internuclear distances and hence $\kappa_{el}^0 \delta r$ also arise between aquo and ammine
complexes in homogeneous electron-transfer reactions, the solvating
environments may be sufficiently different to that pertaining to the
present electrochemical reactions[23] to bring other factors to the fore.
Indeed, the larger rate ratios for Co(III) ammine versus aquo reactants
observed at mercury electrodes relative to that obtained with a given
reductant in homogeneous solution[12] suggest that these differences in
$\kappa_{el}^0 \delta r$ may well be smaller in the latter environment. Nevertheless,
the present finding that outer-sphere electrochemical reactions can be
at least marginally nonadiabatic bears a close resemblance to the inter-
pretation of some anion catalytic effects upon homogeneous outer-sphere
reactions between cationic complexes[25] as well as to the results of the recent
ab initio calculations noted above.[2] Similar calculations have yet to be
performed for electron-transfer processes at metal surfaces; they would
provide an invaluable guide to the further interpretation of the
experimental data.

The present results therefore are at variance with a previous suggestion
that the effective electron-tunneling probabilities should be much larger
at metal surfaces due to the multitude of electronic energy states in the
vicinity of the Fermi level that are available for coupling with the
reactant orbitals.[26] Further support to the present findings is given by
our observation that both the unimolecular rate constants and frequency
factors for the electroreduction of pentaamminecobalt(III) bound to a mercury
surface via organic bridges are decreased markedly upon interruption of bond

conjugation in the bridging ligand.[9,27]   These observations serve to highlight the previously neglected role of nonadiabatic electron tunneling in influencing electron-transfer reactivity at electrode surfaces as well as in homogeneous solution.

Acknowledgements

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(21) The effective value of ΔH_i^* is slightly (0.3 kcal. mol^{-1}) larger than the values given in ref. 17 since these were determined by assuming that the frequency factor is slightly temperature dependent as expected from the collision model utilized in ref. 17.

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TABLE I. Kinetic and Thermodynamic Data for the One-Electron Reduction of Cr(III) Complexes at the Mercury-Aqueous Interface at 25°C.

Reactant	Pathway[a]	$-E$ mv. vs sce	k_{ob}[b] cm sec^{-1}	k_{corr}^{os}[c] cm sec^{-1}	K_p[d] cm	k_{et}^{is}[e] sec^{-1}	$k_{corr}^{os}/k_{et}^{is}$ Å
$Cr(NH_3)_5NCS^{2+}$	is	600	1×10^{-5}		2×10^{-5}	0.5	
$Cr(NH_3)_5N_3^{2+}$	os	600	6×10^{-7}	1×10^{-7}			5-10
	is	600	$\sim 5 \times 10^{-7}$		5×10^{-7}	~ 1	
$Cr(NH_3)_5Cl^{2+}$	os	600	3×10^{-6}	6×10^{-7}			~ 5
	is	600	1×10^{-5}		$\sim 1 \times 10^{-6}$	~ 10	
$Cr(OH_2)_6^{3+}$	os	655	7.5×10^{-6}	2.5×10^{-6}			
$Cr(OH_2)_5SO_4^{+}$	os	705	4.6×10^{-6}	3.5×10^{-6}			~ 0.1-0.3
$Cr(OH_2)_5F^{2+}$	os	860	6×10^{-6}	2×10^{-6}			
$Cr(OH_2)_5NCS^{2+}$	is	720	4×10^{-3}		$\sim 4 \times 10^{-6}$	1×10^{3}	
$Cr(OH_2)_5N_3^{2+}$	is	~ 720	1.2×10^{-4}		$\sim 2 \times 10^{-7}$	2×10^{3}	

[a] is = inner-sphere (ligand-bridged) pathway; os = outer-sphere pathway

[b] Observed rate constant for overall electrode reaction following is or os pathway indicated at electrode potential, E, listed in adjacent column. Values of k_{ob} for Cr(III) aquo complexes determined at formal potential for Cr(III)/(II) couple. Data taken from refs. 5a, 6 and 7.

[c] Work-corrected rate constant for outer-sphere pathway. Determined from corresponding value of k_{ob} using $k_{corr}^{os} = k_{ob} \exp[(Z-0.5)\phi_{rp}]$, where Z is the reactant charge number, and ϕ_{rp} is the average potential at the reaction plane (see refs 6 and 7 for details).

[d] Stability constant for the inner-sphere precursor state, determined from Eq (7); taken from ref. 5a.

[e] Unimolecular rate constant for electron-transfer step involving ligand-bridged intermediate. Obtained from listed values of k_{ob} and K_p using Eq. (2).

Figure Caption

Schematic plot of electronic transmission coefficient κ_{el} for an outer-sphere electrochemical reaction against the reactant-electrode separation distance r. A'A" and B'B" represent anticipated planes of closest approach for Cr(III) ammine and aquo, reactants, respectively. The shaded and cross-hatched areas represent the corresponding values of the "effective reaction zone thickness" $\kappa_{el}^{o} \delta r_{e}$ for these reactants.

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